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Simulation of Nutrient Loss From Soils Due to Rainfall Acidity

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This paper describes a simulation model that provides a quantitative system utilizing established relationships from soil chemistry to predict the most likely effect of rainfall acidity on the leaching of cations from noncalcareous soils.

The model utilizes the relationships between lime potential (pH - 1/2pCa) and base saturation described by Clark and Hill (Soil Sci. Soc. Amer. Proc. 28:490-492, 1962) and Turner and Clark (Soil Sci. 99:194-199, 1964), the equilibrium between CO_2 partial pressure and H^+ and HCO_3^- in solution, the apparent solubility product of $AL(OH)_3$, the equilibrium of cations and anions in solution, the Freundlich isotherm description of sulfate adsorption, and mass balance considerations, to predict the distribution of ions between the solution and sorbed or exchangeable phases. Ionic composition of leachates in response to rainfall composition can thus be computed. Ions considered in the present version are H^+, Ca^{2+}, Al^{3+}, SO_4^{2-}, CL^-, and HCO_3^-.

The model predicts almost exact chemical equivalence between basic cation removed in the leachate and strong acid anions entering the system in the rainfall if pH - 1/2pCa is above 3.0, at which point the base saturation will generally not exceed 20%. At lower pH - 1/2pCa values leaching of anions in association with H^+ and Al^{3+} becomes significant and these cations predominate when pH - 1/2pCa falls below 2.0.

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SIMULATION OF NUTRIENT LOSS FROM SOILS DUE TO RAINFALL ACIDITY

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FOREWORD

Effective regulatory and enforcement actions by the Environmental Protection Agency would be virtually impossible without sound scientific data on pollutants and their impact on environmental stability and human health. Responsibility for building this data base has been assigned to EPA's Office of Research and Development and its 15 major field installations, one of which is the Corvallis Environmental Research Laboratory (CERL).

The primary mission of the Corvallis Laboratory is research on the effects of environmental pollutants on terrestrial, freshwater, and marine ecosystems; the behavior, effects and control of pollutants in lake systems; and the development of predictive models on the movement of pollutants in the biosphere.

This report describes a simulation model designed to predict the impact of rainfall acidity on the leaching of cations from non-calcareous soils. This work was undertaken as a part of a research program at CERL to determine the effects of acid rain on forest ecosystems.

A. F. Bartsch
Director, CERL

ABSTRACT

This paper describes a simulation model that provides a quantitative system utilizing established relationships from soil chemistry to predict the most likely effect of rainfall acidity on the leaching of cations from non-calcareous soils.

The model utilizes the relationships between lime potential (pH - 1/2pCa) and base saturation described by Clark and Hill (Soil Sci. Soc. Amer. Proc. 28:490-492, 1962) and Turner and Clark (Soil Sci. 99:194-199, 1964), the equilibrium between CO_2 partial pressure and H^+ and HCO_3^- in solution, the apparent solubility product of $Al(OH)_3$, the equilibrium of cations and anions in solution, the Freundlich isotherm description of sulfate adsorption, and mass balance considerations, to predict the distribution of ions between the solution and sorbed or exchangeable phases. Ionic composition of leachates in response to rainfall composition can thus be computed. Ions considered in the present version are H^+, Ca^{2+}, Al^{3+}, SO_4^{2-}, Cl^-, and HCO_3^-.

The model predicts almost exact chemical equivalence between basic cation removed in the leachate and strong acid anions entering the system in the rainfall if pH - 1/2pCa is above 3.0, at which point the base saturation will generally not exceed 20%. At lower pH - 1/2pCa values leaching of anions in association with H^+ and Al^{3+} becomes significant and these cations predominate when pH - 1/2pCa falls below 2.0.

If the soil exhibits sulfate adsorption properties, leaching of bases in response to rainfall containing sulfuric acid may be delayed until a sulfate adsorption equilibrium is reached, but base removal would continue after the sulfuric acid input was stopped.

Most of the work reported here was completed while the author was on assignment as a soil chemist at the Corvallis Environmental Research Laboratory, Corvallis, Oregon.

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An extra measure of thanks are due to Mr. J. Warren Hart who's efforts and skills in programming, mathematics, and chemistry contributed substantially to the successful planning of the program.

SECTION 1

INTRODUCTION

The trend toward increased rainfall acidity over northern and western Europe and the northeastern United States appears well established. This in turn is causing concern about the possibility of accelerated losses of mineral bases from soils and subsequent losses of productivity (Anon., 1971; Jonsson and Sundberg, 1972). However, ion exchange properties in soils are complex, and cation losses from soils due to leaching by acid rainfall is modified by soil properties (Wiklander, 1974; Mälmer and Nilsson, 1972).

This paper describes a model that calculates ion loss from soils as a function of soil properties and of the composition and distribution of rainfall. The objective of the model is to provide a quantitative system that utilizes established principles of soil chemistry to predict the most likely effect of rainfall acidity on leaching of basic cations from non-calcareous soils. It must be regarded as preliminary due to the limited number of ions considered and numerous simplifying assumptions. Nonetheless, in my opinion, the model provides the most reliable method presently available for estimating the effect of rainfall composition on losses of bases from soils. It also provides the basic structure that can be used in subsequent models incorporating additional ions and processes.

SECTION 2

CONCLUSIONS

It is entirely feasible to simulate the ion exchange and removal processes that are likely to occur in soils as a consequence of rainfall acidity. Known physical-chemical relationships coupled with simulation techniques combine to give the best prediction presently possible of long term effects that are not amenable to experimental measurements within a reasonable length of time. The following specific conclusions were arrived at by a first generation model of this type that applies only to non-calcareous soils.

The initial results of these investigations indicate that significant acidification and depletion of bases could occur over a period of a few decades if rainfall inputs are consistently acidified to pH 4.0 with sulfuric acid.

We can expect almost an exact chemical equivalency between strong acid anion content of rainfall and leaching of bases from soils with base saturation levels above about 20%. As base saturation becomes lower the leaching will diminish and then cease but the exact nature of this relationship must await further investigation.

Leachate composition will initially be controlled largely by the anion concentration of the rainfall, and will be independent of whether the rainfall cations are mineral bases or H^+. The long term base status of the soils will, however, respond to the cation composition of the rainfall.

Soils with a significant capacity to adsorb sulfates will tend to dampen the effect of sulfuric acid induced leaching of basic cations. The leaching of bases will respond more slowly to acidic imputs than on non-sulfate adsorbing soils but will reach a similar equilibrium rate of leaching as the sulfate adsorption capacity reaches equilibrium with the rainfall sulfate. On these

soils high rates of leaching induced by rainfall containing sulfuric acid could be expected to persist for some time after acid rainfall input ceased.

Soil pH as measured by soil water suspensions may be markedly lowered by increased rainfall ion concentrations. This rapid change is a result of rainfall anion concentration and would occur in a similar manner in response to rainfall containing either strong acids or neutral salt.

Soil pH as measured by soil water suspension is well known to vary with time. However, the predictions given by the model show clearly the effect of seasonal precipitation-evaporation relationships of a magnitude of about 2.5 times the overall change that would be expected to occur in a decade in response to pH 4.0 rainfall. Experiments that depend on soil water extract or suspension pH measurements to evaluate the effect of acid rainfall inputs would be subject to serious errors due to these fluctuations.

The long term leaching of cations in response to rainfall acidity will be largely independent of the precipitation/evaporation ratio as long as periodic leaching occurs.

Cation removal in response to rainfall mineral composition will be largely independent of CO_2 partial pressure.

The initial model results indicate that base removal due to rainfall acidity from actual soil systems can validly be investigated on an experimental basis by increasing the acidity of applied water to levels in excess of that normally found in rain. This would shorten the time necessary to investigate base removal. Measurement of pH on soil water suspensions from such experiments would not be valid as much lower values would be expected than would occur if the weaker acid were applied for the longer time periods.

SECTION 3

RECOMMENDATIONS

Simulation modelling based on known physical-chemical relationships in soil offers the most feasible method of evaluating long term effects of acid rainfall on the base status of soils. The model reported here is useful in this regard but is limited by the inclusion of only part of the important ions and by simplifying assumptions concerning water movement in soils. The relationships are sufficiently understood to develop a more complete model including additional ions and more sophisticated water movement relationships. Such a model should be developed immediately.

At the same time laboratory work with soil suspensions and soil columns should be undertaken for experimental verification of the model. If results coincide with model predictions it will add confidence to model prediction of long term effects not easily amenable to direct experimentation. If predictions of laboratory systems do not give acceptable precision, hopefully the reason can be discerned and the model modified accordingly.

The model should also be used to simulate on-going field experimentation, both to validate the model, and to determine if the procedure used in the field trials can reasonably be expected to give reliable and useful results.

SECTION 4

MODEL STRUCTURE AND THEORY

GENERAL DESCRIPTION

A general schematic representation of the model is shown in Fig. 1. The model was developed using a daily time step. Data supplied on a daily basis from external sources include rainfall and evapotranspiration in millimeters, and the concentration of Ca^{2+}, H^{+}, Cl^{-}, and SO_4^{2-} ions (moles/liter) in the rain. The present form of the model has been restricted to these ions plus HCO_3^{-}, and Al^{3+}. Various initial conditions must be specified at the start of each run and these will be pointed out in the discussion of the soil processes.

After the rain has entered the soil composition of the soil water is recalculated based on previous water content, constituents added, and evapotranspiration. The ionic equilibria are then calculated and a new solution concentration is established for each ion. If the new water content is greater than field capacity, the excess is removed as leachate, which is assumed to have the same composition as the soil solution. The total amounts of Ca^{2+}, SO_4^{2-}, and Cl^{-} ions in the system are specified initially. The amount entering in the rain is known from the input data and the amount lost in the leachate at each time step are calculated within the model, so the total sorbed plus solution amount of each ion is known at all times.

EQUILIBRIUM PROCESSES

The equilibrium between solution ions and sorbed ions is the principle focus of the model. In the initial stages it was assumed that the soil-solution and atmosphere-solution equilibria were uniform to the depth being considered and all results reported are from this version. Later revisions include the capabilities of considering various depth layers with different soil properties separately.

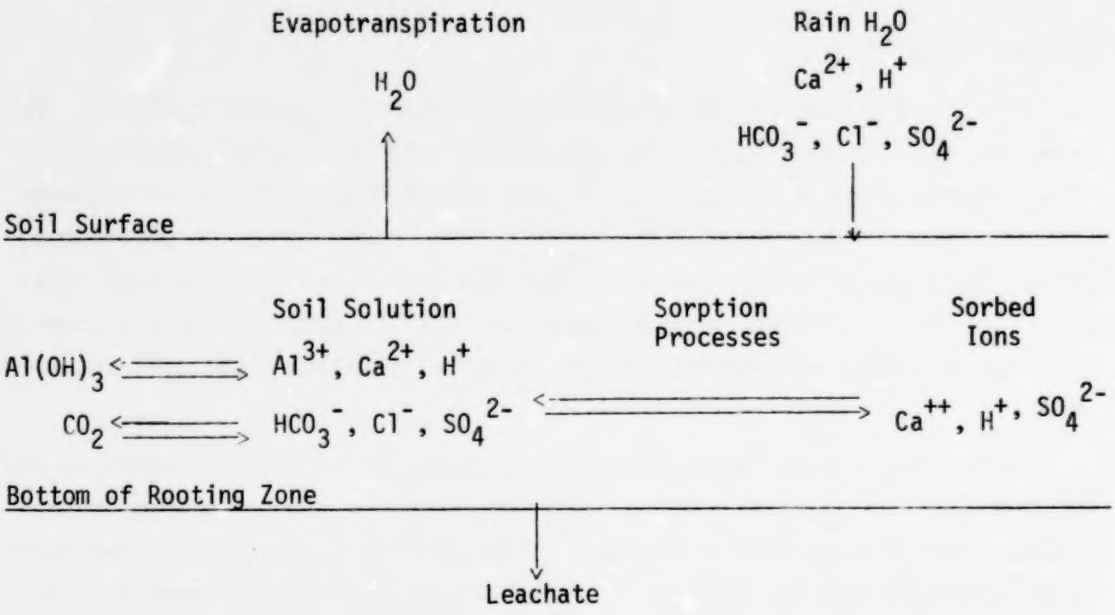

Figure 1. Generalized diagram of model describing the interaction of rainfall chemistry with soil solution processes.

Sulfate Adsorption

Soils exhibit the phenomenon known as sulfate adsorption to varying degrees. Sulfate adsorption is commonly encountered in acid soils, particularly those that are highly weathered and contain iron and aluminum sesquioxides. Haward and Reisenauer (1965) discuss possible mechanisms of sulfate adsorption processes. Whatever the mechanism, soils that adsorb sulfate tend to maintain an equilibrium between SO_4^{2-} in solution and that sorbed onto soil surfaces.

$$SO_4^{2-} \text{ (solution)} \rightleftharpoons SO_4^{2-} \text{ (sorbed)}$$

Various expressions have been used to describe this equilibrium, including the Freundlich and Langmuir adsorption isotherms (Chao et al., 1962; Hasan et al., 1970)

I have chosen to describe the SO_4^{2-} adsorption process in the model with the Langmuir equation which is used in the form:

$$SO_4^{2-} \text{ (sorbed)} = \frac{K_{max}\,[SO_4^{2-}]}{k_{\frac{1}{2}} + [SO_4^{2-}]} \qquad (1)$$

Where $[SO_4^{2-}]$ is the equilibrium sulfate concentration in moles/liter, K_{max} is the adsorption maximum, i.e., moles SO_4^{2-} adsorbed per unit of soil at infinite $[SO_4^{2-}]$, and $k_{\frac{1}{2}}$ is related to the bonding energy and is the $[SO_4^{2-}]$ at which SO_4^{2-} adsorbed is equal to one-half K_{max}. Total SO_4^{2-} is always known and consists of the sum of the sorbed and solution components so that:

$$SO_4^{2-} \text{ (total)} = SO_4^{2-} \text{ (sorbed)} + SO_4^{2-} \; \theta \; D \qquad (2)$$

Where θ is the volumetric moisture content (liters water/liter soil) and D is the depth in millimeters of the soil profile simulated. The units of SO_4^{2-} sorbed and SO_4^{2-} total as used in the model are moles per square meter to depth D. Equations (1) and (2) are sufficient to define the distribution of total sulfate between the solution and sorbed phases, and this distribution is calculated in the model at each time step prior to calculating the concentration of the remaining ions as described below.

These calculations depend on the availability of values of K_{max} and $k_{\frac{1}{2}}$ for any soils to be simulated. Many soils adsorb very little sulfate and can be

simulated by simply inserting very low values for K_{max}. Literature values are available for a number of typical sulfate adsorbing soils (Chao et al., 1962; Hasan et al., 1970).

Chao et al. (1962) point out the limitations of the Langmuir isotherm. The soils they studied did not exhibit appropriate adsorption maximas, even though they did follow the relationship over a substantial range from which an "adsorption maxima" could be predicted. Hasan et al. (1970) refer to this as a "first phase adsorption maxima." Thus for any particular soil simulated, the relationships in the model are only valid for the range of sulfate adsorption within which the Langmuir relationship is valid. In addition it should be understood that the SO_4^{2-} concentration in (1) might better be expressed in terms of activity. However, the literature values available are generally in terms of concentration so no activity coefficients are applied to SO_4^{2-} in the model.

Ca - H Equilibria

In order to define the H^+ and Ca^{2+} exchange equilibria, I chose to utilize the concept of "Lime Potential" of Schofield and Taylor (1955). Soil pH measurements are highly sensitive to factors such as dilution and salt effects, but these authors demonstrated that the Lime Potential, defined as $pH - \frac{1}{2}p(Ca + Mg)$, is remarkably constant for a given soil even though soil water content may vary widely. With changes in water content the shifts between exchangeable and solution Ca^{2+} and H^+ are such that K_L remains constant. In our system where Mg is not presently considered we can write:

$$pH - \tfrac{1}{2}pCa = K_L \qquad (3)$$

K_L, the Lime Potential, can easily be determined for any given soil by measuring the pH and the activity of the Ca^{2+} ion in a suspension of soil. pH and pCa are defined as the negative logarithms to the base 10 of the H^+ and Ca^{2+} activities respectively.

The relationship in (3) is sufficient for our purposes if only short term simulations are used. However, if losses or gains of calcium are significant the fraction of exchange sites occupied by Ca^{2+} (base saturation) changes so that K_L changes also. It appears, however, that K_L can be satisfactorily rel-

ated to base saturation as shown by Clark and Hill (1964). In our system, the only base considered is calcium, so base saturation V is defined by (4).

$$V = \frac{2CaX}{CEC} \tag{4}$$

Where CaX is the moles of exchangeable Ca per unit of soil and CEC is the cation exchange capacity in equivalents. If we accept the relationships found by Clark and Hill (1964), (Fig. 2) one for montmorillonitic soils, and the other for more weathered soils, we can write:

$$pH - \tfrac{1}{2}pCa = f(\frac{CaX}{CEC}) \tag{5}$$

Where $f(\frac{CaX}{CEC})$ is the function shown in Fig. 2 for the soil we wish to simulate. In the program coordinates of the points on the appropriate curves are furnished as data and intermediate points are calculated by linear interpolation as required.

Some care is required in the interpretation of Fig. 2 due to the manner in which CEC is defined. Clark and Hill refer to this as "permanent", i.e. non-pH dependent, charge. In reality in highly base saturated soils, some pH dependent charge would be included. Thus, if a highly base saturated soil is acidified, CEC may decrease. Simulations resulting in large changes in base saturation could be subject to error from this effect.

In addition to the relationships shown in (5), the total Ca^{2+} in the simulated system is always known, so that:

$$Ca^{2+}_{total} = CaX + [Ca^{2+}] \ominus D \tag{6}$$

Where Ca^{2+} is the solution concentration in moles/liter, and CaX is the exchangeable Ca in moles/m^2 to whatever depth is considered, and D is expressed in millimeters.

Chemical Equilibria

In addition to the above, certain chemical conditions must be satisfied. In soils above pH 5.0 the HCO_3^- ion may be an important constituent. The concentration of this ion is controlled by CO_2 partial pressure such that:

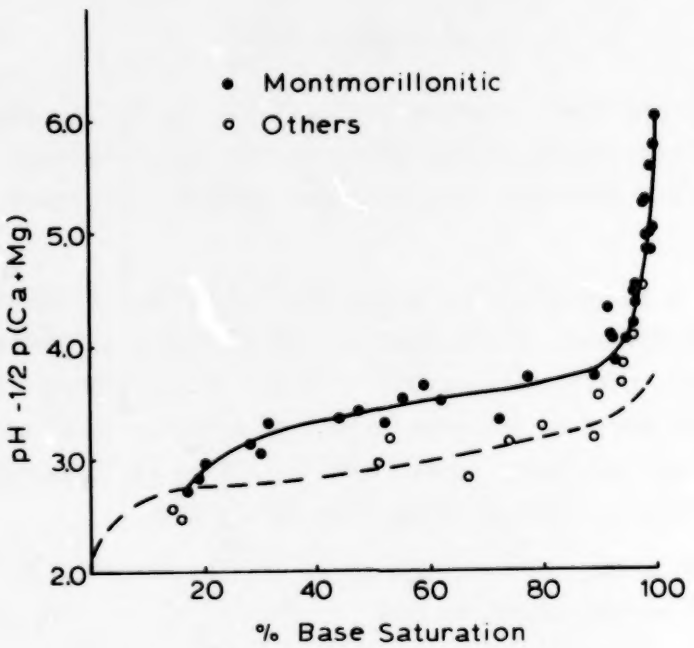

Figure 2. The pH - ½p(Ca + Mg) values of soils as a function of base saturation based on the sum of cations extracted with 1N KCl. (Redrawn from Clark and Hill, 1964).

$$(H^+)\ (HCO_3^-) = (CO_2) \cdot 10^{-7.81} \qquad (7)$$

Where $(CO_2)_g$ is the partial pressure of CO_2 in atmospheres, and (H^+) and (HCO_3^-) are the activities of the two ions in moles/liter. In the model the CO_2 partial pressure must be specified initially.

In acid soils Al^{3+} may be one of the major cations in the system, and neglecting this ion results in unacceptable errors in the predicted H^+ and Ca^{2+} solution concentrations. From the solubility product of $Al(OH)_3$ we can write:

$$(Al^{3+})\ (OH^-)^3 = K_{Al}$$

and substituting $\frac{10^{-14}}{(H^+)}$ for (OH) we obtain eq. (8).

$$(Al^{3+})\ \left(\frac{10^{-14}}{(H^+)}\right)^3 = K_{Al} \qquad (8)$$

In soils the K_{Al} would represent the apparent solubility product for $Al(OH)_3$ which may vary depending on the degree of weathering. For the system simulated here, values of $10^{-33.4}$ to $10^{-33.8}$ were used (Turner and Clark, 1964; Turner, Nichol and Brydon, 1963).

In order to maintain electrical neutrality in the system the total equivalents of anions and cations in the solution must be equal, so that:

$$[H^+] + 2[Ca^{2+}] + 3[Al^{3+}] = 2[SO_4^{2-}] + [HCO_3^-] + [Cl^-] \qquad (9)$$

The brackets again indicate molar concentrations. In this system Cl^- is presumed to exist only in solution, so that when the initial amount is specified and the gain in rainfall and losses in leachate are all known, the amount present at each time step can be calculated.

If we examine eqs. (5) through (9), we find the following parameters are either known or specified; CEC, $f(\frac{CaX}{CEC})$, Ca^{2+}_{total}, Θ, D, $(CO_2)_g$, $[SO_4^{2-}]$ and $[Cl^-]$. The unknowns are (Ca^{2+}), (H^+), $[Ca^{2+}]$, CaX, (HCO_3^-), $[HCO_3^-]$, $[H^+]$ and (Al^{3+}). If for the moment we consider activities ( ) to be equal to concentrations [ ], we have only $[Ca^{2+}]$, $[Al^{3+}]$, $[H^+]$, $[HCO_3^-]$, and CaX as

unknowns.

The five equations in five unknowns define the system, so by solving this set we could calculate the solution concentrations of Ca^{2+}, H^+, Al^{3+}, HCO_3^-, and the exchangeable Ca^{2+}.

An assumption that activities and concentrations are equal is not acceptable, particularly in relation to the tri-valent Al^{3+} ion. It is necessary, therefore, to calculate the activity coefficients γ_1, γ_2, γ_3, where:

$$\gamma_1 \text{ [Concentration]} = \text{(activity)} \tag{10}$$

The Debye-Hückel Theory is used to calculate these coefficients in a manner similar to that utilized by Dutt et al., (1972).

$$\log \gamma_i = \frac{-.509 Z_i^2 \mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} \tag{11}$$

Where Z is the valence and:

$$\mu = \tfrac{1}{2} \sum_{i=1}^{n} C_i Z_i^2 \tag{12}$$

Where n is the total number of ion species present, and C_i is the concentration of each ion.

Equations (1) through (12) are sufficient to define the solution concentrations of the ions considered as well as the amounts sorbed provided the total amounts of input and output are known. Thus by devising a solution to this set of relationships it is possible to predict the changes that will take place as a result of any rainfall composition, provided the amount and distribution of rainfall and the evapotranspirations are known.

Some caution is necessary in interpreting ion concentration or activities as calculated from these equations, particularly in terms of (H^+) or pH. The ion activities reported here as calculated from the above equations should represent those found in the solution phase, commonly referred to as the "outer solution." The boundary between "inner solution" or sorbed phase and "outer solution" may not be well defined and pH measurements made on soil suspensions or pastes are generally lower than those of the extract or supernatant solution due to the influence of this "inner" phase. Probably the best interpre-

tation of the pH values calculated by the program would be those of an extract from a paste or suspension prepared from the indicated soil:water ratio.

MODEL STRUCTURE

Numerical Solutions

The heart of the model is the numerical solution of sets of equations describing sorption and chemical equilibria. The system utilized evolved during development of the model and is probably not the most efficient that could be devised. However, it works well and the processor time required is moderate, even for long term simulations. A brief description of the approach seems appropriate.

First the activity of Al^{3+} is calculated from eq. (8) and the value of (H^+) is taken from the previous time step or iteration. If no previous value of (H^+) is available, a value is assumed. The solution and sorbed SO_4^{2-} are then calculated using eq. (1) and (2). Activity coefficients are calculated using eq. (11) and (12) and previous concentrations or if none are available activity coefficients are assumed for the first iteration.

Next, an iterative method is used for solving equations (5), (6), (7), and (9). This solution is the most complicated in the model. Equations were successively eliminated by substitution and rearranged until one complicated expression of the form $f(H^+) = 0$ was obtained. This is solved by an adaptation of Newton's method. The value of $f(H^+)$ for an assumed value of (H^+) is calculated and the derivative of $f(H^+)$ is evaluated. A new estimate of (H^+) is obtained by projecting the tangent to the abcissa. The processes are repeated until the change in the value of (H^+) is within limits prescribed by the operator. In our simulation this change must be $<10^{-6}$ times the new value of H^+. In the initial equilibration, the program assumes a trial value of (H^+), but in subsequent equilibrations the value from the previous time step is used. Special precautions are taken to avoid estimates for which f(H) is nonexistent and to avoid divergence. When convergence is satisfactory, new values are calculated for CaX and the concentration and activities of Ca^{2+} and HCO_3^-. The program then returns to the calculation of (Al^{3+}), $[SO_4^{2-}]$ and activity coefficients. The process is repeated until the changes in the activity coefficients between successive iterations are within prescribed limits.

General Structure

A generalized flow diagram is shown in Fig. 3. Some of the steps shown in this diagram, particularly the equilibrium calculations discussed above, are quite complex and have their own internal flow patterns.

First the initial conditions are read. These include; constants for SO_4^{2-} adsorption, K_{AL}, depth, CEC, initial water content, field capacity, permanent wilting points, total SO_4, total Ca^{2+}, and total Cl^- in the soil, and CO_2 partial pressure. Coordinates of points for the pH - ½pCa as a function of base saturation relationship are also read as data, as are the limits allowed for the checks of convergence.

The initial equilibria are then calculated for any five specified water contents, and the ion concentrations printed. The initial ion concentration at field capacity defines the initial concentration in the leachate.

If actual rainfall simulations are desired, rainfall is added. Rainfall of any selected composition is presently added in a preset pattern but actual rainfall and evaporation could be read from a data file. After daily rainfall is added, evapotranspiration is subracted unless this would reduce soil water content below the permanent wilting point in which case soil water content is set at the permanent wilting point.

The program provides for printed output at preset intervals. If the date is one for which printed output is required, the procedure is as follows: First, a check is performed to determine whether total water is above field capacity, and if not, no leaching will occur and the program skips directly to the output section. If leaching will occur, the ion equilibration routines are utilized to determine solution concentration. Water in excess of field capacity is removed, and the amounts of ions removed are accumulated. The program then moves to the output routines in which the equilibration routines are called for the preset output water contents; and the concentrations, the accumulated amounts of ions added and leached, and the present amounts of sorbed ions are printed. The program then updates base saturation, checks for end of run and returns to add the next day's rain.

On days when no print is required, the system is simpler; if water content is below field capacity, no further calculation is required and the program

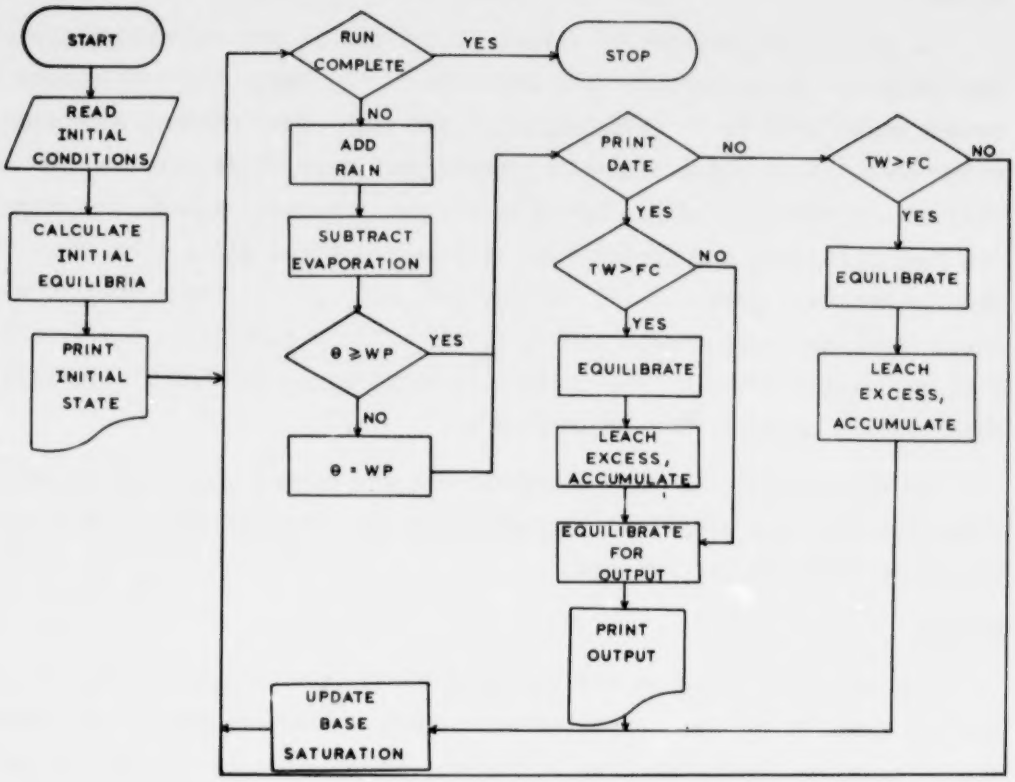

Figure 3. Flow diagram for model of the rainfall chemistry-soil solution system.

returns to check for end of run and rainfall addition. If field capacity is exceeded, new ion equilibria are calculated, the solution in excess of field capacity is removed, and the amounts of water and ions lost are accumulated. Base saturation is updated, end of run is checked and the next days rain is added.

Output

As mentioned previously, output is printed at pre-selected intervals. For the output to be comparable from one time to the next, it is necessary for the output equilibria to be calculated for the same water content each time. Also, water contents at which laboratory measurements of pH or solution ion concentration are made may vary. For this reason, provison is made for output of ion concentrations and sorbed ions at five specified water contents. The volumetric moisture contents (Θ) desired are entered. In these runs, I have used field capacity, approximate saturation (2 x field capacity); and 1:1, 1:5 and 1:10 soil:water ratios. The latter was obtained by setting Θ such that bulk density/Θ is equal to the desired ratio.

In addition to the ion concentrations and sorbed ions, the accumulated water and the ions added and leached since the start of the run and during the preceding interval are printed.

Coding

The model is coded in the standard FORTRAN IV computer language. For the version used in the runs reported here, core memory requirement was about 70000 (octal). Execution time is minimal and by placing a compiled version on a system file, processor charges on the system utilized were less than $2 for a ten year simulation run.

SECTION 5

SIMULATION RESULTS

SHORT-TERM SIMULATIONS

One of the most important applications of the model is for short-term runs in which the ion input-output relationships can be examined as a function of soil and rainfall characteristics. These simulations provide a basis for understanding how cation loss due to acid rainfall is influenced by soil properties.

Non-Sulfate Adsorbing Systems

First, we shall examine results of short-term simulations of a soil system with very low sulfate adsorbing capacity. These runs were made simulating rainfall varying in pH from 3.00 to 6.35 with CO_2 at 3×10^{-4} atmospheres. The ionic composition of the rain is shown in Table 1. The pH - ½pCa values of the soil were varied from 1.5 to 4.0, corresponding to soils that are nearly base saturated (4.0) and extending below the levels normally expected in soils. The pH - ½pCa values were not allowed to change during a run. No evaporation was allowed and steady state conditions were required, i.e., the SO_4^{2-} and Cl^- concentrations were in equilibrium with those of the rainfall and did not change during the run.

Under these conditions, soil solution pH was markedly affected by changing composition of the rain. The results for pH - ½pCa = 3.0 are shown in Fig. 4. This should not be interpreted as due to rainfall acidity but rather to a "salt effect". This can easily be demonstrated with the model by replacing the "acid rainfall" with a $CaSO_4$ rainfall in which the Ca^{2+} concentration is adjusted to equal the sum of the SO_4^{2-} plus Cl^- (in equivalents per liter). Such rainfall would be essentially neutral but the effect on soil pH is almost identical to that of acid rainfall of the same anion concentration. A conceptual model of this effect is that an increase in anion concentration

TABLE 1. Ion concentrations in rainfall used in simulation runs.

No.	pH*	Ca^{2+}	SO_4^{2-}	Cl	log $[SO_4^{2-} + Cl^-]$
		micro equivalents/liter			-log (eq/liter)
1.	3.00	30	1010	40	2.99
2.	3.50	30	330	40	3.46
3.	4.00	30	110	40	3.89
4.	4.49	30	42	40	4.21
5.	4.98	30	20	40	4.40
6.	5.67	30	10	40	4.52
7.	6.35	30	0	40	4.70

*pH at 3×10^{-4} atm CO_2

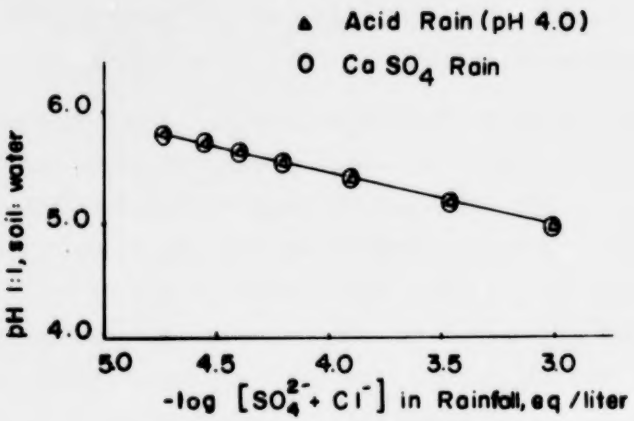

Figure 4. Model prediction of pH of a 1:1 soil:water extract in a soil with pH - ½pCa = 3.0 as a function of $[SO_4^{2-} + Cl^-]$ concentration in rainfall. Circles represent Ca^{2+} as rainfall while X's represent pH 4.0 rain as shown in Table 1. The soil does not adsorb SO_4^{2-} and leachate volume is equal to rainfall.

in solution requires a corresponding increase in cation concentration, including H^+. A soil solution with very low anion concentration could not be highly acidic.

Another characteristic observed in these short-term simulations was that the concentration of Ca^{2+} in the leachate was strictly dependent on the $SO_4^{2-} + Cl^-$ concentration of the rainfall regardless of whether the rainfall cation was Ca^{2+} or H^+. The net change in Ca^{2+} in the soil, of course, was markedly affected by the balance of Ca^{2+} and H^+ in the rain.

Fig. 5 shows a plot of the log of the Ca^{2+} concentration in the leachate as a function of the log of the anion concentration of the rainfall. Note that at pH - ½pCa = 3.0, the Ca^{2+} concentration of the leachate is almost identical to the rainfall anion concentration over the range of $10^{-3.0}$ to $10^{-4.2}$ equivalents per liter. At pH - ½pCa above 3.0 and rainfall concentrations below $10^{-4.0}$ equivalents per liter the leachate Ca^{2++} concentration is greater than the sum of the $SO_4^{2-} + Cl^-$ due to significant amounts of HCO_3^-. As pH - ½pCa drops to 2.0, the leachate Ca^{2+} is substantially lower than the rainfall anion concentration, indicating that H^+ and Al^{3+} are significant components of the leachate.

The actual ratio of Ca^{2+} leached per strong acid anion input in the rain (eq/eq) is shown in Fig. 6. Here, values greater than 1.0 indicate leaching in association with HCO_3^- while values less than 1.0 indicate strong acid anions leached in association with H^+ and Al^{3+}. Note that the basic cations removed are approximately equal to anion input at pH - ½pCa = 3.0. At rainfall ion concentrations relevant to the acid rain system (greater than about $10^{-4.2}$ eq./liter) even at pH - ½pCa = 2.5 the Ca^{2+} leached amounts to about 80% of the anion input, but Ca^{2+} leaching drops off very rapidly as pH - ½pCa is lowered to 2.0. A comparison of these values with the curves in Fig. 2 indicates that we would expect almost a stochiometric 1:1 removal of bases except on soils of very low base saturation, perhaps less than 20% of permanent charge. However, as base saturation is further depleted, the Ca^{2+} removal would decrease rapidly and for the pH 4.00 rainfall shown in Table 1, the Ca^{2+} input would equal the amount leached at about pH - ½pCa = 1.9.

An important consideration is the effect of evapotranspiration. If evapo-

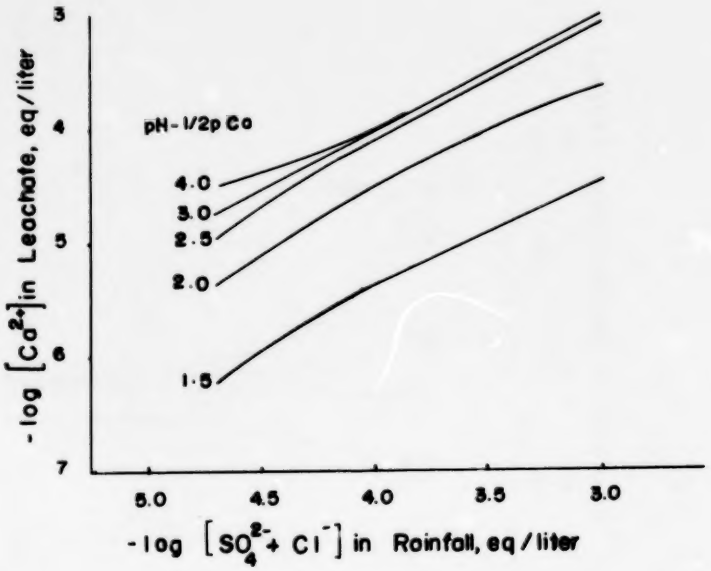

Figure 5. Model prediction of concentration of Ca^{2+} in leachate as a function of $[SO_4^{2-} + Cl^-]$ concentration in rainfall and pH - ½pCa of the soil. The soil does not adsorb SO_4^{2-} and leachate volume is equal to rainfall.

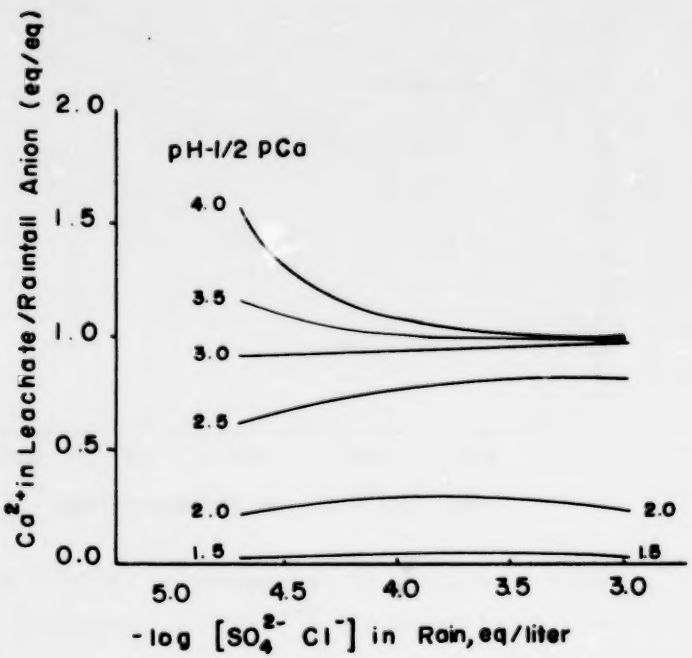

Figure 6. Ratio of Ca^{2+} in leachate per $[SO_4^{2-} + Cl^-]$ in rainfall (eq/eq), as a function of anion strength of rainfall and pH - ½pCa. Soil does not adsorb sulfate.

transpiration is always greater than rainfall, removal is zero and the system accumulates ions from the rainfall. In the previous simulation, evapotranspiration was assumed to be zero. When evaporation occurs the effect is to concentrate the soil solution and decrease the amount of leachate. The implications of this concentrating effect on base leaching were demonstrated by simulating systems in which 10 liters/m^2 of rainfall per day were applied with no evaporation. After equilibrium the evaporation was changed to 9 liters per day, resulting in leaching dropping from 10 to 1 liters per day. In these runs base saturation was held constant to avoid confounding the effect of evaporation. When evaporation was started, the Ca^{2+} leached per unit of rain immediately decreased due to the decrease in amount of leachate (Fig. 7). The soil leachate than started to become more concentrated until a new equilibrium with soil solution was established. In the case shown (pH - ½pCa = 2.5), field capacity = 0.30 and depth = 300 millimeters. This new equilibrium was reached in about 1000 days, at which time the Ca^{2+} leached per unit of rain was only very slightly higher (10.34×10^{-5} vs. 10.22×10^{-5} eq/liter) than in the system where no evaporation was allowed. If evaporation was decreased instead of increased, a period of increased base loss per unit of rainfall was obtained, and the resultant plot is virtually the inverse of that shown in Fig. 7.

Only a few experiments were conducted with the model in which partial pressure of CO_2 was a variable. Results of one of these (Table 2) show that at pH - ½pCa = 3.0 changing CO_2 from 3×10^{-4} to 3×10^{-3} atmospheres had very little effect on soil pH or on leaching of Ca^{2+}. However, at pH - ½pCa = 4.0 and 4.5 leaching of Ca^{2+} increased by 33 and 78%, respectively, with the increase in CO_2. Increased leaching of Ca^{2+} leached due to CO_2 was accompanied by an equivalent increase in HCO_3^- in the leachate. Apparently changes in Ca^{2+} leaching due to the strong acid anions in the rainfall are virtually independent of CO_2 partial pressure. Leaching of cations in association with HCO_3^- seems to be relatively unimportant when pH - ½pCa is 3.5 or less but at pH - ½pCa levels above 4.0 it becomes the major factor, particularly if the rainfall is non-acidic.

Sulfate Adsorbing System

The effects of sulfate adsorption on base removal by acid rainfall as pre-

Table 2. Effect of CO_2 partial pressure on extract pH and on Ca^{2+} leached using simulated pH 4.0 rainfall.

pH - ½pCa	CO_2 (atm)	pH, 1:1	Ca leached	
			meq/m^2	% change
3.0	3×10^{-4}	5.41	12.28	4
	3×10^{-3}	5.36	12.80	
3.5	3×10^{-4}	5.88	12.94	12
	3×10^{-3}	5.77	14.50	
4.0	3×10^{-4}	6.34	13.48	33
	3×10^{-3}	6.16	17.94	
4.5	3×10^{-4}	6.77	14.72	78
	3×10^{-3}	6.52	26.20	

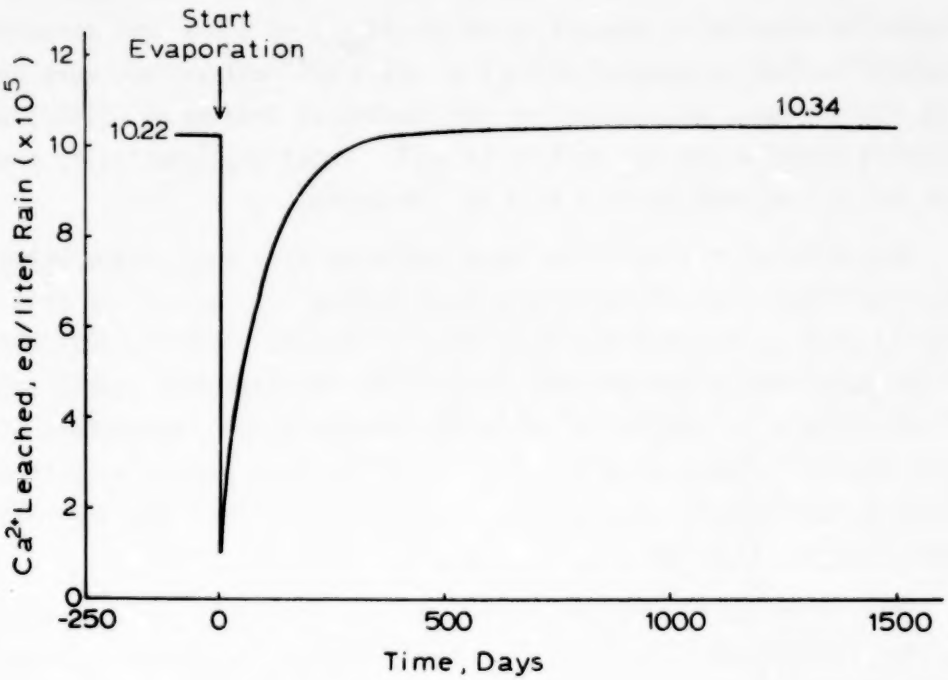

Figure 7. Predicted effect of changing evaporation from 0 to 90% of rainfall on the amount of Ca^{2+} leached from the soil per equivalent of rain. pH - ½pCa was 2.5, rainfall pH 4.0, and there was no adsorption of SO_4^{2-}.

dicted by the model are interesting and important. I know of no experimental results that either support or refute these predictions. Therefore the predictions should be considered as testable hypotheses.

For these short-term simulations involving a soil with significant sulfate adsorption capacity an adsorption maxima (K_{max}) of 3.6×10^{-3} moles/kg and a one-half maximum concentration ($k_{\frac{1}{2}}$) of 1.8×10^{-4} moles/liter were used. These values were calculated from the results of Chao et al. (1962) and approximate their values for an Astoria soil. Total SO_4^{2-} initially present in the soil was assumed to be 3.15×10^{-4} moles/kg.

When short-term simulations were conducted with this system using various characteristics and values of pH - $\frac{1}{2}$pCa ranging from 1.5 to 4.0 (Fig. 8), the results were quite different from those of the non-adsorbing soil (Fig. 5). In the adsorbing system the Ca^{2+} ions in the leachate were nearly independent of the sulfate ion concentration in the rainfall, i.e. independent of sulfuric acid induced rainfall acidity. The reason for this independence is that the solution concentration was largely controlled by the sulfate adsorption properties rather than rainfall.

This independence was temporary, when the input SO_4^{2-} concentration was increased, the adsorbed SO_4^{2-} tended to increase until eventually a new equilibrium was established with a higher solution concentration, and base removal then proceeded at the higher rate.

Conversely, when the solution rainfall input was again lowered, base removal preceeded at a higher rate while sulfate desorption occured. When the evaporation experiment shown in Fig. 7 was conducted using a simulated SO_4^{2-} adsorbing soil, the time required to reach a new equilibrium was increased by several-fold. The actual time, of course, was a function of the specific K_{max} and $k_{\frac{1}{2}}$ of the soil. These effects point out the possibility that with sulfate adsorbing soils, increased base removal may not occur in detectable amounts until stressed with acid rain for long periods, but if the stress is removed, base removal would continue until the adsorbed SO_4^{2-} decreased to equilibrium with the new input level. It should be recognized that these simulations were based on the assumption of complete reversibility of sulfate adsorption. If a portion of the adsorption sites were irreversible the leaching of basic cations after sulfuric acid stress was removed would be less than

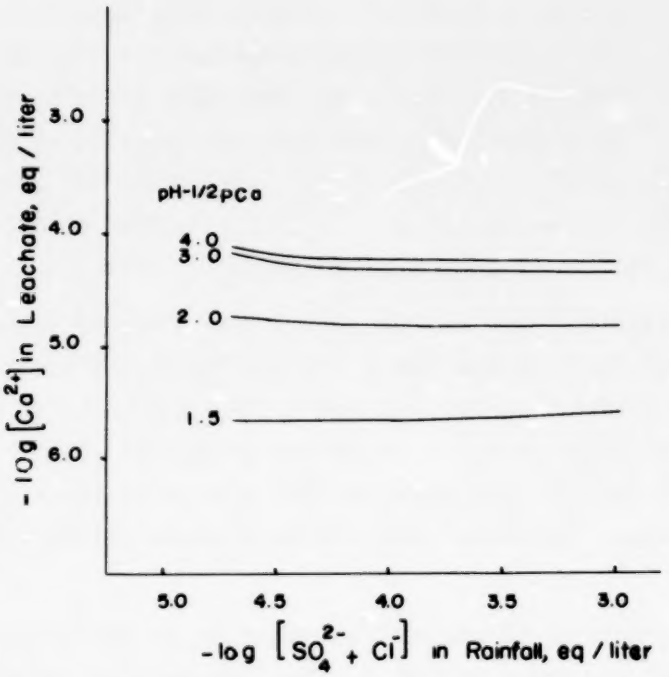

Figure 8. Model prediction of concentrations of Ca^{2+} in leachate of a SO_4^{2-} adsorbing soil as a function of $[SO_4^{2-} + Cl^-]$ and pH - ½pCa. Leachate volume is equal to rainfall.

the equivalent amount of sulfate adsorbed.

LONG-TERM SIMULATIONS

Several longer-term simulations were run with the model. In contrast to the results reported above, in these cases base saturation and pH - ½pCa were allowed to respond to gains or losses in Ca^{2+}. Results are reported for two runs, one assuming sulfate adsorption properties similar to those of the Astoria soil (Chao et al., 1962), and the other assuming very low sulfate adsorption. The initial base saturation was low (20% of permanent change), and the relationship of pH - ½pCa to base saturation was that shown by the lower line (montmorillonitic soils) of Fig. 2. Initial conditions and soil properties used in these simulations are shown in Table 3.

The rainfall used was the pH 4.0 rain shown in Table 1. A total of 1100 mm rain per year was simulated, one-twelfth of which was applied each month. The pattern within months included 13 days per month in which rain occured in amounts varying from 1.1 to 22 mm/day (Table 4). Potential evapotranspiration rates were changed each month and are typical of those in the northeastern United States. Potential evaporation exceeded rainfall for the May - Sept. period.

The predicted solution pH values of a 1:1 soil-water system for a five-year period are shown in Fig. 9. The seasonal fluctuations predicted are of the order of .25 pH units for the non-adsorbing soil. This results from changes in solute concentration due to the lack of leaching during the summer period when evapotranspiration exceeds rainfall. The increased solute concentration decreases pH due to the "salt effect" discussed previously. In the SO_4^{2-} adsorbing soil these fluctuations are much smaller. This damping effect is due to the control the SO_4^{2-} adsorption exerts on solution anion concentration.

Measurements of pH in soil water suspensions or leachates often vary markedly with time (Russel, 1961 p 105; Cole and Ballard, 1970). Smooth seasonal fluctuations such as are observed in the model output are rare, but actual rainfall and leaching patterns are also highly variable between seasons. The effects demonstrated by the model are undoubtedly a major factor in inducing fluctuations. Effects of this magnitude are probably realistic and could constitute a major source of error in experiments attempting to measure field pH changes due to acid rainfall inputs.

Table 3. Initial conditions and soil properties for a 10-year acid rainfall simulation

	SO_4^{2-} Adsorbing Soil	Non-adsorbing Soil
Cation Exchange Capacity (eq/kg)	0.10	0.10
Initial Base Saturation (%)	20.00	20.00
Depth (meters)	0.30	0.30
Field Capacity (% volume)	30.00	30.00
Permanent Wilting Point (% volume)	12.50	12.50
Bulk Density (kg/liter)	1.25	1.25
CO_2 Partial Pressure (atm)	3×10^{-4}	3×10^{-4}
SO_4^{2-} Adsorption		
K_{max} (moles/kg)	3.6×10^{-3}	3.6×10^{-5}
$k_{\frac{1}{2}}$ (moles/liter)	1.8×10^{-4}	1.8×10^{-3}
Initial S (moles/kg)	8.56×10^{-5}	1.42×10^{-5}
K_{sp} - $Al(OH)_3$	$10^{-33.8}$	$10^{-33.8}$

Table 4. Rainfall and evapotranspiration patterns used for 10-year simulations

Month	Potential Evapotranspiration		Rainfall
	mm/day	mm/month	mm/month
Jan.	.033	1.0	91.7
Feb.	.067	2.0	91.7
March	.533	16.0	91.7
April	1.533	46.0	91.7
May	3.067	92.0	91.7
June	4.367	131.0	91.7
July	5.133	154.0	91.7
Aug.	4.533	136.0	91.7
Sept.	3.323	100.0	91.7
Oct.	1.767	53.0	91.7
Nov.	.633	19.0	91.7
Dec.	.100	3.0	91.7
			1100.4

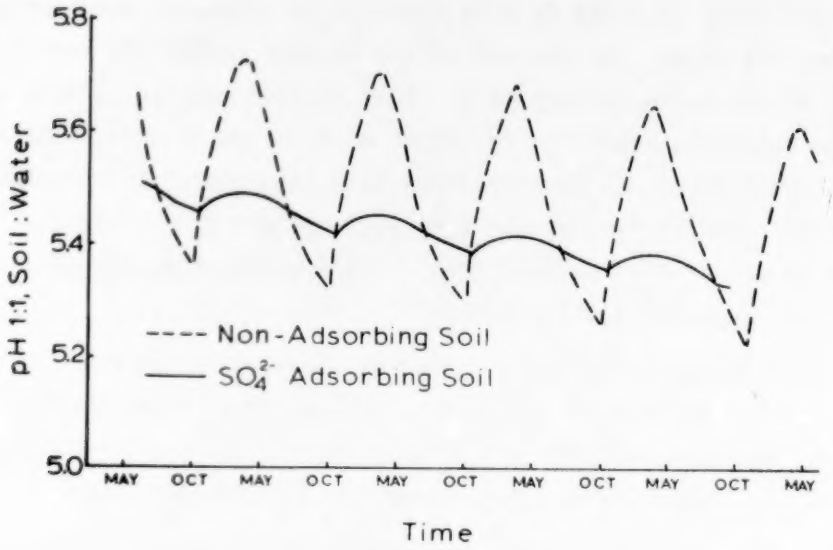

Figure 9. Simulated time-based fluctuations in soil pH using pH 4.0 rainfall.

The total (exchangeable plus solution) Ca^{2+} in the system dropped in a stepwise pattern (Fig. 10). A small gain occured during the summer due to rainfall inputs with no leaching. This was followed by a sharp drop in the fall. In this case the loss was lower for the sulfate adsorbing soil than for the non-adsorbing soil, but in the adsorbing soil the loss increased slightly each year. This increase is more apparent in Figure 11 where only the April 30 values are shown. By the end of the 10-year period the loss rate approached that of the non-adsorbing soil. This occured because sulfate was adsorbed from the rainfall, resulting in higher equilibrium solution concentrations. While these effects may be of considerable importance, the graphs must be interpreted with caution as the base loss pattern of sulfate adsorbing soils depends on the initial sulfate level. It appears, however, that adsorption dampens the seasonal oscillations.

An interesting effect is observed in the plot of solution pH values on April 30 (Fig. 12). Even though less Ca^{2+} was lost from the SO_4^{2-} adsorbing soil than the non-adsorbing soil, the pH of the soil-water suspension dropped at a slightly faster rate. The reason for this is not clear.

The net change in soil Ca^{2+} per equivalent of excess acidity in the rainfall is about 98% at the start and 96% at the end of the ten-year period for the non-adsorbing soil. Base saturation decreased from 20% to 17.12%. Further declines in base saturation would rapidly decrease the Ca^{2+} loss per unit of H^+ added. More precise information on the nature of the functional relationship between base saturation and pH - $\frac{1}{2}$pCa is required to simulate more accurately the effects in this region.

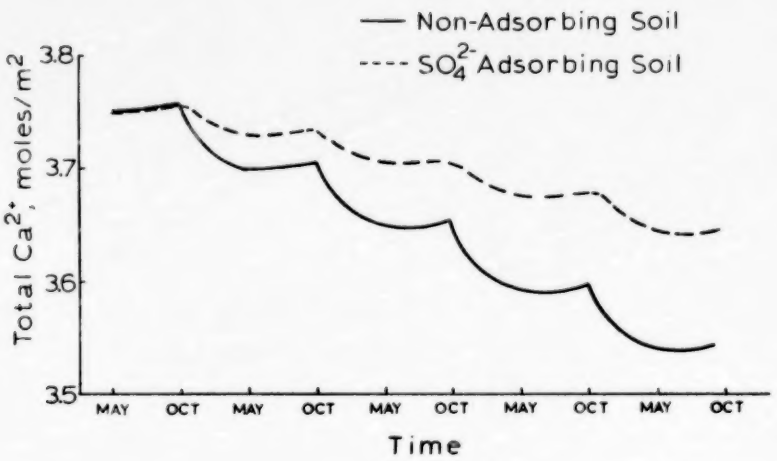

Figure 10. Simulated change in total Ca^{2+} (soluble plus exchangeable) in 0.3 meters of soil during a 5-year period using pH 4.0 rainfall.

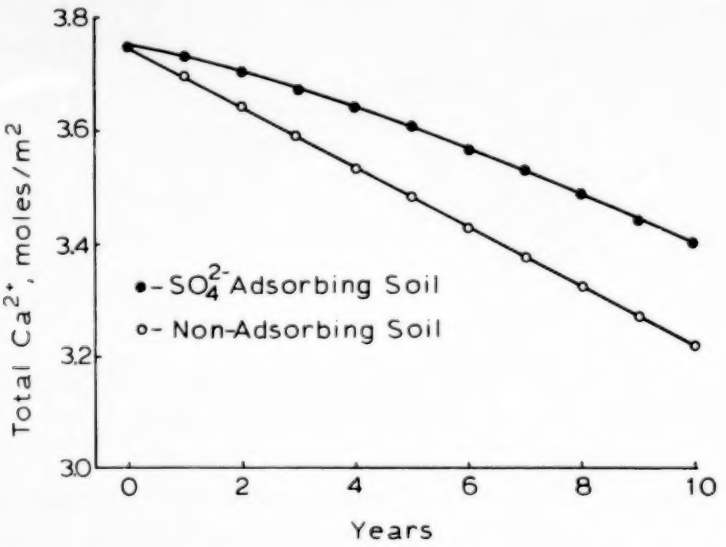

Figure 11. Simulated total Ca^{2+} found on April 30 in 0.3 meters of soil stresses with pH 4.0 rainfall over a 10-year period.

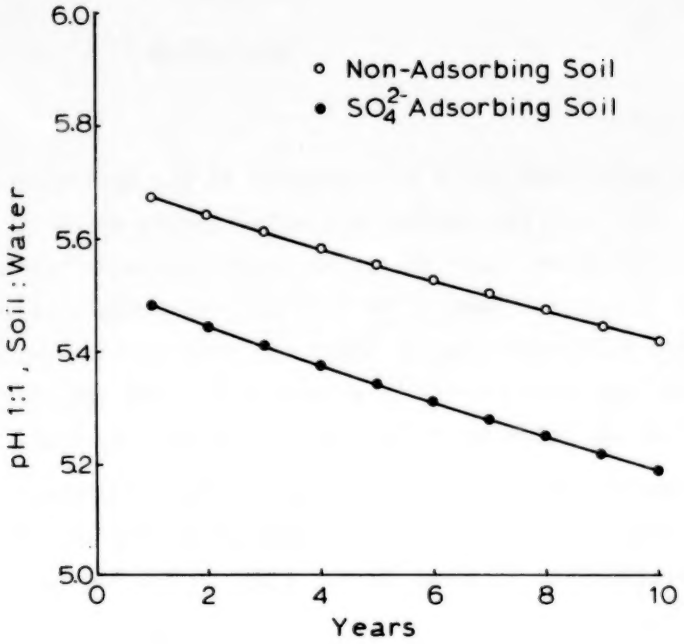

Figure 12. Simulated April 30 1:1 soil:water extract pH values for SO_4^{2-} adsorbing and non-adsorbing soils stressed with pH 4.0 rainfall.

SECTION 6

DISCUSSION

LIMITATIONS

The major limitation of the model is the exclusion of all basic cations except calcium. The system is complex and it appeared desireable to successfully complete and test the model in the present form before attempting to include additional ions. The time and resources alloted to the initial program were fully utilized in completing the version reported here. Fortunately the model has been useful in providing a basic insight into the effect of soil properties on leaching of cations due to acid rainfall.

Inclusion of additional cations should not present any serious difficulties. They can probably bast be handled by the use of the well known Gapon type relationship as shown in eq. (13) - (15) for two component systems.

$$\frac{MgX}{CaX} = C_1 \frac{(Mg^{2+})}{(Ca^{2+})} \tag{13}$$

$$\frac{KX}{CaX} = C_2 \frac{(Na^{+})}{(Ca^{2+} + Mg^{2+})}^{\frac{1}{2}} \tag{14}$$

$$\frac{NaX}{CaX} = C_3 \frac{(Na^{+})}{(Ca^{2+} + Mg^{2+})}^{\frac{1}{2}} \tag{15}$$

Where [MgX]/[CaX], [KX]/[CaX], and [NaX]/[CaX] denote the ratios of these ions on the exchange complex, the ( )'s denote solution activities in moles per liter, and C_1, C_2, and C_3 are constants for which approximations are available in the literature. These relationships plus the concept that the total exchangeable plus soluble amounts of these ions are always known in the model, and the equivalence of soluble anions and cations allow the inclusion of any

or all of these ions. The exchange relationships are the same as those used by Dutt et al. (1972) in their model which is applicable only to calcareous soils.

These relationships have been widely discussed in the soils literature and it is not appropriate to repeat them here. It may be noted that C_1 is generally considered to be less than 1.0, indicating that Mg is less tightly held on the exchange complex than Ca. Beckett (1965), however proposes that certain exchange sites exhibit a specificity for each ion, and that more of these have an affinity for Ca than Mg. After these specific sites are satisfied, the value of C_1 is apparently 1.0.

The situation regarding potassium is interesting. The K^+ ion is generally considered to be more mobile and subject to leaching than Ca^{2+} or Mg^{2+}. Equation (14) indicates that the ratio of exchangeable K^+ to exchangeable Ca^{2+} should be a linear function of the ratio of the activity of K^+ in solution to the square root of the molar activity of Ca^{2+} in solution, or what is commonly termed the activity ratio. This relationship generally appears valid but such plots from actual measured values in soil generally predict a small positive intercept interpreted as being caused by certain exchange sites with a specific affinity for K^+. (Becket et al. 1966). The slopes for the soils these authors used were in the range of 3.25 to 10.4 with apparent intercepts ranging from .006 to .03.

Even though potassium is not specifically included in the model eq. (14) can be used to predict the leaching of K^+ due to acid rain effects in at least a semi-quantitative manner. For instance a typical relationship found by Beckett et al. (1966) was for

$$KX/CaX = 0.008 + 6.0\ (K^+)/(Ca^{2+} + Mg^{2+})^{\frac{1}{2}} \qquad (16)$$

The cation exchange capacity was 0.27 equivalents per kilogram and the base saturation approximated 75%. Using the lower line of Fig. 2 we would predict a pH - ½pCa value of about 3.0. If we consider this to be a two component system of K^+ and Ca^{2+}, the exchangeable Ca would be about 0.20 equivalents per kilogram. Assuming a relatively high exchangeable K^+ of 0.005 we would have a KX/CaX ratio of 0.025. By exposing this soil to a rainfall such as No. 6 in Table 2 having a pH of 5.67 and a log $[SO_4^{2-} + Cl^-]$ of -4.52 we

would expect to have a leachate with log $[Ca^{2+}]$ of -4.52 with no evaporation (fig. 5). Actually the K^+ comprises a significant portion of the cation in the leachate so that log $[Ca^{2+} + K^+] = -4.52$ or $[Ca^{2+}] = 3.16 \times 10^{-5} - K$. For this semiquantitative calculation we can assume activities equal to concentrations and substitute into (16) so that:

$$0.025 = 0.008 + 6(K^+)/(3.16 \times 10^{-5} - (K^+)) \qquad (17)$$

Solving (17) we find $[K^+] = 9.4 \times 10^{-6}$ and $[Ca^{2+}] = 2.2 \times 10^{-5}$.

The ratio of dissolved K/Ca is 0.42, or more than 16 fold the ratio of the exchangeable ions. Surprisingly if this same calculation is carried through for the pH 3.0 rainfall (Table 2), where log $K^+ + Ca^{2+}$ from Fig. 5 is -3.0, the predicted ratio of dissolved K/Ca is 0.067 or only about 2½ times the ratio of the exchangeable ions. Thus K appears to be selectively leached in this system, but the selective removal of K is diminished by the higher ion concentration in the more acid rainfall. Similarly the selectivity of K leaching would be depressed by the concentration effect of evapotranspiration.

As the ratio of exchangeable K/Ca decreases, the selectivity of K leaching also decreases. For rainfall pH 4.0 from Table 2 and assuming no concentration by evapotranspiration we find that at an exchangeable K/Ca ratio of 0.0087, K/Ca ratios would be equal for the solution and exchangeable components. If exchangeable K is depleted below this level, Ca would be selectively leached. It should, however, be noted that equation (16) predicts a zero level of soluble K^+ at an exchangeable K/Ca ratio of 0.008. This apparent intercept is an artifact due to sites that exhibit specificity for K^+ and at very low exchangeable K/Ca levels (16) becomes invalid (Beckett et al., 1966). However, the concept that selective leaching of K^+ in preference to Ca^{2+} ceases and even reverses at very low exchangeable K/Ca ratios remains valid.

The assumption of uniform equilibration throughout the depth of soil considered also imposes limitations. The results of the model in the form used for this report should have general validity but will suffer in applicability to specific situations where various profile depths have widely varying properties. Depth effects can be included by dividing the soil into discrete layers for which successive equilibrations are calculated in the model. Initial conditions must then be supplied for each depth. Precision may also

be added by coupling a soil water model to the exchange equilibrium model in the manner used by Dutt et al. (1972) rather than simply assuming leaching of the soil solution in excess of field capacity.

The relationship of base saturation to Lime Potential utilized here (Clark and Hill, 1964) is highly empirical. Similar curves can be derived on a much more theoretical basis. Turner and Clark (1964) show that the relationship can be described by (18).

$$pH - \tfrac{1}{2}\, p(Ca + Mg) = 1/6 \log \frac{K_{Al}}{K_1 K^6} + 1/6 \log \frac{[CaX + MgX]^3}{[AlX]^2\, CEC} \qquad (18)$$

Where [CaX],[MgX] and [AlX] refer to the exchangeable ions in moles and CEC is the cation exchange capacity in equivalents taken as the sum of the exchangeable Ca, Mg, and Al; the K is the ion product of water of 10^{-14} at 25^{o} C, K_1 is an ion exchange constant for this system determined to be $10^{-1.5}$, and K_{Al} is the solution product $(Al)(OH)^3$. If Mg is not included:

$$CaX = \frac{V}{2}\,(CEC)$$

$$AlX = \frac{CEC\ (1 - V)}{3}$$

Where V is the base saturation.

Eq. (18) can then be written as

$$pH - \tfrac{1}{2}pCa = 1/6 \log \frac{K_{Al}^{\,2}}{10^{-85.5}} + 1/6 \log 9/8 \frac{(V^3)}{(1 - V)^2} \qquad (19)$$

Thus eq. (19) shows a theoretical functional relationship between base saturation and pH - ½pCa, dependent only on the value of K_{Al}. The functional relationships assumed from Fig. 2 and used in the model as eq. (5) could be replaced directly by eq. (19). A more straightforward approach would be to drop MgX and use eq. (18) directly along with (20) which simply states that the equivalents of CaX and AlX add up to the cation exchange capacity.

$$CEC = 3AlX + 2CaX \qquad (20)$$

The eight equations (1), (2), (6), (7), (8), (9), (18), and (20) now form a set in which, (considering activities to be equal to concentrations), the

unknowns are; $SO_{4(sorbed)}$, $[SO_4]$, $[H^+]$, $[Ca^{2+}]$, $[Al^{3+}]$, $[HCO_3^-]$, CaX and AlX. The use of the Lime Potential K_L as a constant or as an empirical function of the base saturation is actually unecessary and the validity of the system is not actually dependent on the "constancy" of the Lime Potential.

Unfortunately, I did not recognize the potential of this approach until its inclusion would have required a major restructuring of the equilibration section of the model so it has not been included in the version reported here.

Controlling solution Al^{3+} in the model by means of an "apparent solubility product" of $Al(OH)_3$ is a vast oversimplification of this equilibrium involving Al. Apparently the two lines in Fig. 2 arise from different $(Al^{3+})(OH^-)^3$ ion products with the values for the montmorillonitic soils generally ranging between $10^{-35.5}$ and $10^{-34.1}$ while most of the non-montmorillonitic soils are in the range of $10^{-34.1}$ to $10^{-32.8}$. This difference rather than any direct effect of the clay type appears to account for the different lines on Fig. 2 (Turner and Clark, 1964). I assume that the lower equilibrium levels of Al^{3+} in the montmorillonitic soils is related to the fact that this clay mineral is generally found in soils that are not highly weathered. For broad scale application of the model it would seem appropriate to investigate whether this ion product can reasonably be predicted by any of the common soil classification schemes.

The model does not take into account the possible release of cations from soil minerals to the exchange complex as a result of weathering processes. In the present form it is not feasible to include this process, but one can imagine a more sophisticated system including equilibria for various Al, Fe, and Si species that would predict rate of weathering and cation release from soils of known mineral composition.

USEFULNESS

Even though several deficiencies of the model are recognized, it is nevertheless extremely useful. The predictions relating to the buffering or dampening effect of soil SO_4^{2-} adsorbing properties are important. Acidity effects such as pH changes or cation leaching could lag well behind the acid inputs of the rainfall due to this mechanism, but increased base removal would continue after the acidity inputs ceased.

It is often assumed that soils with low pH and low basic cation contents would be highly susceptible to atmospheric chemical influence (Jonsson and Sundberg 1972). The fallacy of this viewpoint has been previously pointed out (Wiklander 1973; Wiklander 1974; Malmer and Nilsson 1972). The output of this model confirms that soils well supplied with bases are most susceptible to base loss and that as base saturation and lime potential fall to low levels acid precipitation causes leaching of H^+ and Al^{3+} ions rather than bases. Unfortunately this transition takes place at very low base saturation levels, as base removal is almost equivalent to rainfall acidity inputs at 20% base saturation or above.

The obvious method of evaluating rainfall acidity effects in the field is to measure pH changes. Several of the problems with this approach are apparent from the output of this model. For instance the imposition of acid rainfall may immediately lower the measured pH value simply due to higher anion content, even though a similar effect would occur due to addition of rainfall containing a neutral salt, or as a result of concentration of salts found in rainfall by evapotranspiration effects. The seasonal effects on pH shown in the model are striking. Unfortunately, in nature these are not smooth annual cycles but are highly irregular. Cole and Ballard (1968) show a variation of 0.3 pH units in drainage water through the forest flow over a period of about 4 hours, the pH decreased as conductivity increased as would be expected from the present model. The acidic characteristics are further complicated by biotic uptake and release of both anions and cations. These processes affect the acid base status of the soils (Reuss 1977). Changes in more fundamental soil properties such as pH - $\frac{1}{2}$pCa or pH - 1/3pAl are much more likely to give meaningful measures of the effect of external acidity imposed on soils than are pH measurements.

The initial output from the model indicates that loss of bases from the system in response to rainfall acidity could be significant when considered on a time scale of several decades. The system simulated would have lost about 0.5 moles Ca^{2+} per square meter over a decade when subjected to pH 4.0 rainfall at a rate of 1100 millimeters per year. While subject to wide annual variation the downward trend in solution pH of a 1:1 soil water system was proceeding at a rate in excess of 0.1 units per decade for a soil with the

properties chosen for simulation.

One method of shortening the time necessary for field investigations of the effect of rainfall acidity is to apply highly acid artificial rainfall. The model output indicates a reasonable prediction of base removal due to ion exchange effects, at least to the extent of inputs at pH 3.0 which was the lower limit of the test run. This can be discerned from the fact that the lines on Fig. 6 are nearly horizontal in the region where rainfall pH values are below about 4.0. Caution should be observed in interpreting pH values from such investigations, as highly acid artificial rainfall would increase the solution ion concentration and pH measurements on the common water suspensions would be unrealistically depressed.

The model is strictly abiotic and does not take into account biological processes of any type. It could be very logically used, however, as a module in a more comprehensive ecosystem nutrient cycling model.

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